DYNAMIC SIMULATION OF BULK POLYMERISATION OF STYRENE USING ODE SOLVER WITHIN MATLAB SOFTWARE

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NOMENCLATURE

a	Density of reacting mixture
A_d	Pre-exponential Factor Initiator Decomposition, 1.58 x 10^{15} s^{-1}
A_p	Pre-exponential Factor for Propagation, 1.1051 x 10^{7} l/gmol-s
A_t	Pre-exponential Factor for Termination, 1.255 x 10^{9} l/gmol-s
C	Initiator Conversion, kmol/m^3
D	Parameter in Gel Effect Equation
E_d	Activation Energy for Initiator Decomposition, 30800 cal/gmol
E_p	Activation Energy for Propagation, 7060 cal/gmol
E_t	Activation Energy for Termination, 1680 cal/gmol
f	Initiator Efficiency, 0.6
I_o	Initial Initiator Concentration, mol/l
I	Initiator Concentration, mol/l
k_d	Kinetic Constant for Initiator Decompostion, s^{-1}
k_p	Kinetic Constant for Propagation, l/gmol-s
k_{po}	Kinetic Constant for Propagation, l/gmol-s
k_t	Kinetic Constant for Termination, l/g-mol-s
k_{to}	Initial Kinetic Constant for Termination, m^3/kmol-s
k_n	Rate Expression for Styrene Model Equations, n = 1, 2…
$k_{\theta p}$	Parameter in Gel Effect Equation, s^{-1}
$k_{\theta t}$	Parameter in Gel Effect Equation, s^{-1}

M_o	Initiator Monomer Concentration of Styrene, 8.7006 mol/l
M	Monomer Concentration of Styrene, mol/l
MW_m	Molecular Weight of Monomer, 0.10415kg/mol
m	Monomer Conversion (ξ_1)
PD	Polydispersity
R_g	Universal Gas Constant, 1.987 cal/gmol-K
X_n	Number Average Molecular Weight
X_w	Weight Average Molecular Weight
$t0$	Initial Batch time, 0s
t_f	Final Batch Time, s
T	Temperature reaction, 373K
T_{gp}	Glass Transition Temperature, 373K
ξ_0	Zeroth Moment of Dead Polymer, dimensionless
ξ_1	First Moment of Dead Polymer, dimensionless
ξ_2	Second Moment of Dead Polymer, dimensionless
ρ_p	Density of Polymer, 1060kg/m^3
μ_1	First Active Moment of Polymer, dimensionless
$Ø_p$	Volume Fraction of Polymer, dimensionless

SIMULASI DINAMIK PEMPOLIMERAN PUKAL STIRENA DENGAN MENGGUNAKAN PENYELESAI ODE DALAM PERISIAN MATLAB

ABSTRAK

Tajuk kajian ini adalah untuk membangunkan simulasi dinamik pempolimeran pukal stirena dengan menggunakan penyelesai ODE dalam perisian MATLAB. Objektif-objektik kajian ini adalah untuk membangunkan penyelidikan simulasi pempolimeran pukal stirena bersama dengan pemangkin 2,2' azobisisobutyronitrile (AIBN) dalam kelompok reaktor dengan menggunakan penyelesai ODE dalam perisian MATLAB dan juga untuk menentukan jumlah awal kumpulan pemula (AIBN) yang diperlukan dan masa untuk menghasilkan nilai penukaran monomer (*m*) dan bilangan purata berat molekul (*Xn*) yang diingini pada 373K suhu tetap. Hasil kajian simulasi dalam kajian ini menggunakan perisian MATLAB dibandingkan dengan hasil yang diperolehi oleh Wan Ibrahim (2011) dengan mengunakan CVP teknik dalam perisian gPROMS dan juga hasil yang diperolehi oleh Ekpo (2006). Persamaan model dibangunkan dan diguna pakai dalam kajian ini adalah serupa dengan yang digunakan oleh Wan Ibrahim (2011) dan Ekpo (2006) dan persamaan model ini dianggap sebagai masalah nilai awal ODE dan diselesaikan dengan menggunakan penyelesai ODE15s dalam perisian MATLAB. Trend keputusan menunjukkan bahawa masa untuk penukaran monomer (*m*) yang lebih rendah adalah lebih rendah berbanding dengan masa untuk penukaran monomer (*m)* yang lebih tinggi bagi setiap bilangan purata berat molekul (*Xn*). Jumlah awal kumpulan pemula yang dicapai dalam kajian ini adalah lebih rendah berbanding dengan jumlah awal kumpulan pemula yang diperolehi oleh Ekpo (2006), tetapi masa yang dicapai dalam kajian ini adalah berbeza-beza berbanding dengan masa yang dicapai oleh Ekpo (2006). Berbanding dengan keputusan yang diperolehi oleh Wan Ibrahim (2011), jumlah awal kumpulan pemula yang diperlukan dalam kajian ini adalah lebih rendah daripada jumlah awal kumpulan pemula yang diperlukan dalam Wan Ibrahim (2011) kajian, tetapi masa dicapai dalam kajian ini adalah lebih panjang berbanding dengan masa yang diperolehi oleh Wan Ibrahim (2011). Kesimpulannya, penggunaan penyelesai ODE dalam perisian MATLAB dalam simulasi masalah dinamik pempolimeran pukal stirena adalah berjaya. Jumlah awal

kumpulan pemula dan masa dapat ditentukan dan keputusan yang dicapai dapat bersaing dengan keputusan yang diperolehi oleh Wan Ibrahim (2011) dan Ekpo (2006). Walau bagaimanapun, ia adalah disyorkan bahawa kajian masa depan boleh dijalankan dengan mempertimbangkan kesan rantaian pemindahan dan suhu optimum dalam kajian yang menggunakan kaedah yang sama dan perisian.

DYNAMIC SIMULATION OF BULK POLYMERISATION OF STYRENE USING ODE SOLVER WITHIN MATLAB SOFTWARE

ABSTRACT

The title of this study was to investigate the dynamic simulation of bulk polymerisation of styrene using ODE solver within MATLAB software. The objectives of this study were to develop the a simulation research on bulk polymerisation of styrene using 2,2' azobisisobutyronitrile catalyst (AIBN) catalyst in batch reactor by using ODE solver within MATLAB software and to determine the initial amount of initiator and batch time to yield desired values of monomer conversion (m) and the number average molecular weight (X_n) at fixed temperature 373K. The results later on were compared with those obtained by Wan Ibrahim (2011) using CVP technique within gPROMS software and also the results obtained by Ekpo (2006). The model equations were developed and adapted similar to those used by Wan Ibrahim (2011) and Ekpo (2006). The model equations were posed as initial value ODE problems and solved using ODE15s solver within MATLAB software. The trend of results showed that the batch time for lower monomer conversion (m) was lower compared to the batch time for higher monomer conversion (m) for each number average molecular weight (X_n). The initial amount of initiator achieved in this study was lower compared to that obtained by Ekpo (2006) but the batch time achieved in this study varied with that obtained by Ekpo (2006). Comparing with the results obtained by Wan Ibrahim (2011), initial initiator concentration needed in this study was lower than that needed in Wan Ibrahim (2011)'s study, but the batch time achieved in this study was much higher compared to that obtained by Wan Ibrahim (2011). As a conclusion, the use of ODE solver within MATLAB software in simulating the dynamic problem of bulk polymerisation of styrene was successful. The initial amount of initiator and batch time was able to be determined and the results achieved were able to compete with the results obtained by Wan Ibrahim (2011) and Ekpo (2006). However, it was recommended that the future study could be done by considering the chain transfer effect and optimal temperature in the study using the same method and software.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Plastics are true man-made materials and these polymers have played an important role in the development of human modern civilization (Campo, 2008). Among all other polymers, polystyrene is one of the most manufactured polymers in the world from food packaging and housewares items to more durable plastic parts used in industries (Ekpo & Mujtaba, 2004; Li et al., 2011). Li et al. (2011) further stated that 8% of the world polymer market is polystyrene, featuring good stiffness, transparency and excellent processability compared to other polymers and especially rubber. Kiparissides (1996) stated that the future of polymer manufacturing industries is brighter and more exciting with the development and researches of advanced mechanistic models, molecular property estimation, model-based predictive control and optimisation of process operations in recent years. Özkan et al. (1998) and Kiparissides (2006) agreed and further emphasized that recent developments on process modeling, optimisation and control will bring important effects towards polymer plant operability and economic.

1.2 PROBLEM STATEMENT

In today's marketplace where competition among polystyrene manufacturers are high due to the marvelous profits returned in polystyrene business. Tarafder et al. (2004) stated that a small improvement in the plant operation will significantly affect the production cost, which in turn will benefit the consumers as well. According to Gao et al. (2004), the cost of polystyrene production in batch process can be lowered by minimising the batch time meanwhile maintaining molecular weight distribution of the final polymer in a desired range. Ekpo and Mujtaba (2004) agreed and stated that optimisation in polystyrene production will definitely generate billions-Euro-a-year money. Hence, it is desirable to produce polystyrene with lower cost in industrials. In this paper, an ODE (ordinary differential equation) solver available within the MATLAB (Matrix Laboratory) software was used to simulate and investigate the initial amount of initiator towards batch time of bulk polymerisation of styrene.

1.3 RESEARCH OBJECTIVES

This study outlined the following objectives:

a) To develop a simulation research on bulk polymerisation of styrene in batch reactor by using ODE solvers within MATLAB software.

b) To determine the initial initiator and batch time to yield specific values of monomer conversion (m) and the number average molecular weight (X_n) at fixed temperature.

c) To compare the results in this study using MATLAB software with the results using gPROMS (general Process Modeling System) software in Wan Ibrahim (2011)'s study.

1.4 SCOPES OF STUDY

The scopes of this research were discussed below:

a) Simulation researches of bulk polymerisation of styrene using 2,2' azobisisobutyronitrile catalyst (AIBN) as initiator in a batch reactor.

b) Initial amount of initiator and its effect on monomer conversion (m), the number average of molecular weight (X_n) and batch time.

c) Model equations in solving the simulation problem. The problem was posed as Nonlinear Programming (NLP) problem using ODE (ordinary differential equation) solvers available within the MATLAB software.

1.5 SIGNIFICANCES OF STUDY

A model which was Control Vector Parameterisation (CVP) technique had been developed and discussed in recent works. Ekpo and Mutjaba (2004) used this technique to simulate the dynamic optimisation of styrene polymerisation in batch reactors. Wan Ibrahim (2011) further improved the work from Ekpo and Mutjaba (2004) and compared the results by using gPROMS software.

Here, the significance of this study was that the researcher of this study used ODE solvers within MATLAB software to run simulation researches on the bulk polymerisation of styrene in a batch reactor using the same model equations in Wan Ibrahim (2011)'s study. If the simulation researches were successful, it signified that MATLAB software was also capable and suitable to solve any optimisation problems instead of CVP technique within gPROMS software in the future works.

Besides that, it was important to understand the effect of initial initiator on batch time in the polymerisation process while still maintaining monomer conversion and number average of molecular weight of the final polymer in a desired range. This was because the batch time would determine the polystyrene production cost and also the yield of polystyrene production in industries.

1.6 OVERVIEW OF THE STUDY

This study comprised of five main chapters including introduction in Chapter 1. Literature reviews on related researches had been discussed in Chapter 2 while Chapter 3, discussed on mathematical model development and MATLAB software computation development. Chapter 4 discussed on the dynamic simulation problem formulation and results and discussion while the last chapter reviewed on the conclusion of the study and recommendations. This study was completed with references and appendices for better understanding on the research.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter provided a literature review on the dynamic simulation of bulk polymerization of styrene using 2,2' azobisisobutyronitrile catalyst (AIBN) as initiator in a batch reactor using ODE solver within MATLAB software. Topics discussions included introduction to polymer and monomer, polymerisation process in batch reactor and lastly dynamic simulation methods. All the information could be obtained from books, articles and journals.

2.2 INTRODUCTION TO POLYMER AND MONOMER

Polymers are a group of materials that are built up of long covalently-bonded molecules, where these molecules are composed of individual units, called monomers (Nicholson, 2006; Painter & Coleman, 1997; Young & Lovell, 1991).

Polymers consist usually of multiple structural units from hundreds to more than tens of thousands, and these units are bounded together by covalent bonds (Helgesen, 2011; Odian, 2004).

The process by linking together monomer molecules is known as polymerisation and this process will be discussed further later. According to Young and Lovell (1991), the long chain which sets polymer apart from other materials will determine and give rise to the polymer characteristic properties. In this research, a type of monomer, styrene was introduced to bind chemically to form a polymer, polystyrene through polymerisation process. The figures below show general form of styrene and polystyrene.

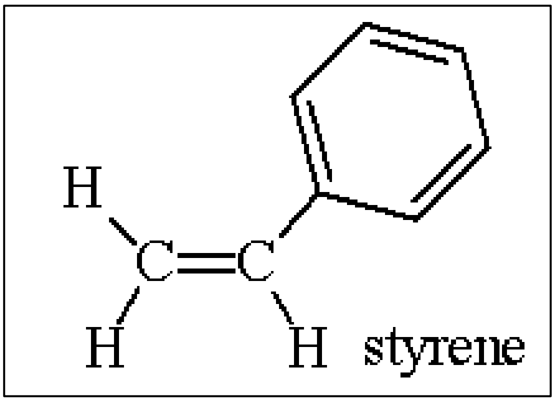

Figure 2.1 Styrene Monomer

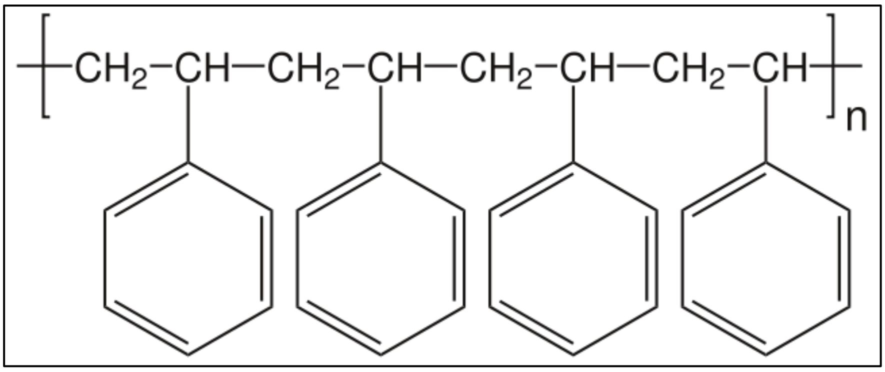

Figure 2.2 General Form of Polystyrene (n = number of repeating units)

2.2.1 Styrene and Its Properties

Styrene is an important monomer in the world where its products are used in an increasingly wide range of applications. According to Product Safety Bulletin (2007), 49 % of the world production of styrene monomer is consumed to produce polystyrene based on 2004 data. It is an organic compound with the chemical formula $C_6H_5CH=CH_2$ or C_8H_8. The C_6H_5 group also makes styrene known as vinyl benzene and phenyl ethene. The presence of the vinyl group allows styrene to polymerise to form polystyrene. Figure 2.1 shows styrene monomer.

There are some properties of styrene. Firstly, it is a colorless oily liquid that evaporates easily and has a sweet smell (Nicholson, 2006). The odor threshold for styrene is 0.32 parts per million (ppm) or 4.26 mg/m^3. Its molecular weight is 104.16 g/mol. The vapor pressure for styrene is 5 mm Hg at 20 ℃, and its octanol/water partition coefficient (log K_{ow}) is 2.95. Styrene is slightly soluble in water, soluble in ethanol and very soluble in benzene and petroleum ether. Table below shows some of styrene monomer physical properties.

Table 2.1 Styrene Monomer Physical Properties

Styrene Properties	
Molecular formula	C_8H_8
Molar mass	104.15 g/mol
Appearance	colorless oily liquid
Density	0.909 g/cm ^{3}
Melting point	-30 ℃, 243 K, -22 ℉
Boiling point	145 ℃, 418 K, 293 ℉
Solubility in water	< 1%
Refractive index	1.5469
Viscosity	0.762 cP at 20 ℃

2.2.2 Properties of Polystyrene

Commonly, polystyrene is known as 'Styrofoam' and it is used widely in the world due to its inexpensive production cost. In chemical terms, polystyrene is a vinyl polymer, which is made from monomer styrene through polymerisation process. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. Its chemical formula is $(C_8H_8)_n$. Nicholson (2006) stated that polystyrene has excellent colour range, transparency, rigidity, and low water absorption features. Odian (2004) agreed and further stated that polystyrene is a very good electrical insulator, has excellent optical clarity due to the lack of crystallinity, good resistance towards aqueous acids and bases, and is easy to fabricate into products. Figure 2.2 shows the general form of polystyrene where n is the number of monomers.

Polystyrene presents in solid or glassy state at normal temperature. When heated above its glass transition temperature, Polystyrene will deform and turn into a form that flows and can be easily used for molding and extrusion. However, it becomes solid again when temperature drops below its glass transition temperature. Table below shows some properties of general purpose polystyrene polymers.

Table 2.2 Properties of General Purpose Polystyrene Polymers (Campo, 2008)

Polystyrene Properties	
Molecular formula	$(C_8H_8)_n$
Glass transition temperature	100^oC
Specific Gravity	1.05
Melting Temperature, T_m (^oF)	212
Process temperature (^oF)	390-480
Mold Temperature (^oF)	50-175
Drying Temperature (^oF)	160-200
Tensile modulus @ 73^oF (Mpsi)	0.45
Tensile modulus @ yield (kpsi)	6.0

2.2.3 Application of Polymer in Industries

According to Young and Lovell (1991), the use of polymeric materials is increasing rapidly year by year due to their capability in replacing a lot of conventional materials such as metals, wood and natural fibres such as cotton and wool. Besides that, polymer chemistry is continually advancing nowadays. In medicine, polymer is used as device to improve patient health. Examples are artificial heart and peacemakers, machines for artificial kidney dialysis and replacement joints for hips, knees and fingers (Nicholas, 2006). In food packaging industries, Nicholas (2006) further gave some examples of polystyrene such as yoghurt pots, hamburger boxes and plastic cutlery.

One of the polymeric materials, polystyrene is widely used in the word from flimsy foam packaging to more durable plastic parts used in automobiles (Ekpo and Mujtaba, 2004). According to Product Safety Bulletin (2007), polystyrene is used to produce commodity packages and consumer goods, primarily used in insulation, packaging, appliances, furniture, toys and cassettes. The main reason for the researcher of this study chose to research on bulk polymerisation of styrene in producing polystyrene was because of the increasingly significant usage of polystyrene in human daily life.

Figure 2.3 and 2.4 shows some examples of polystyrene products which are polystyrene container and medical mounting plates with functional surfaces.

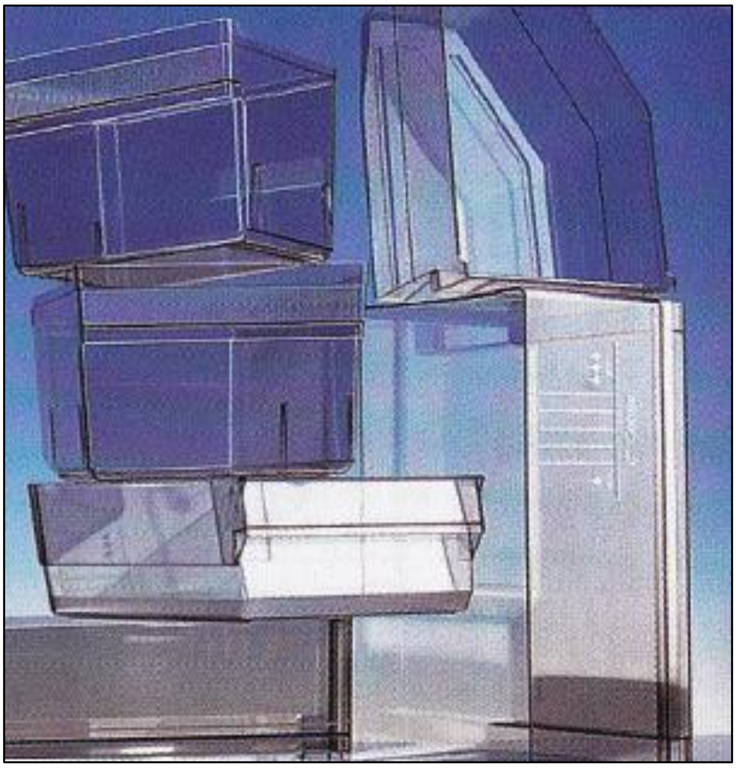

Figure 2.3 Polystyrene Container

Figure 2.4 Medical Mounting Plates with Functional Surfaces